

POLYACRYLAMIDE-SUPPORTED CHROMATES: PREPARATION AND APPLICATION AS A RECYCLABLE OXIDISING AGENT

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ABSTRACT

1, 6 hexanediol diacrylate (HDODA) crosslinked polyacrylamides of different crosslink densities were prepared using potassium persulphate as the radical initiator by free radical solution polymerisation. Transamidation of the HDODA-crosslinked polyacrylamides was done using excess ethylenediamine. The amino functionalised polyacrylamides were converted to Polyacrylamide-supported chromates and maximum functionality was found to be maximum for 10% crosslinked polymer. Polyacrylamide-supported chromates were used for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds. To analyse the effect of reaction conditions on the rate of the reaction, different experimental conditions like varying the solvent, molar excess, temperature and time were used and the studies revealed that the reaction conditions influence the extent of the reaction.

KEYWORDS: Polyacrylamide Supports; Degree of Crosslinking; Chromate Oxidation; Heterogeneous; Polymeric Oxidising Agents & Macromolecular Supports

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1. INTRODUCTION

During the last four decades, organic synthesis mediated by crosslinked polymer supports has been an active area of research. for use in Oxidation^{1,2}, halogenation³, acylation,⁴ catalysis or epoxidation⁵ are different reactions where polymeric reagents have been widely used. Polymeric reagents are more advantageous over the classical solution chemistry because they have the potential advantage of operational simplicity and can help in saving a tremendous amount of time⁶. The relative polarity, porous structure, swelling characteristics, degree of crosslinking, and the topographical nature of the gel network⁷ are the properties used to characterize polymer supports. In the field of metal complexation,^{8,9} dye binding¹⁰ and for the preparation of a number of polymer-supported reagents,¹¹ the design of synthetic polar polymeric supports such as polyacrylamide is a significant achievement¹². The polyacrylamide family of polymers and copolymers is a highly versatile group that represents the extreme of hydrophilic nature.¹³ This article describes the synthesis of 1, 6 hexanediol diacrylate (HDODA) crosslinked polyacrylamide-chromate polymers with varying mole percentages of crosslinking.

2. EXPERIMENTAL

MATERIALS AND METHODS

Hexanedioldiacrylate (HDODA) is a commercial product available from the Aldrich Chemical Company in the United States, and acrylamide was purchased from SRL in Mumbai, India. All low molecular weight compounds are commercially available samples and have been purified by the methods of the literature. The AR grade solvent was purified by distillation. The IR spectrum was recorded with a Schimadzu FTIR8400S spectrophotometer. The UV spectrum was recorded using a Shimadzu UV2450 spectrophotometer. Melting point was measured using

Büchi 530 melting point appliance and ^1H NMR spectroscopy using the BRUKER BZH 500 MHz NMR spectrometer.

Preparation of 2mol% HDODA-Crosslinked Polyacrylamides¹⁴

In 70 ml ethanol, 13.92 g of AA and 0.89 ml of HDODA were dissolved and heated to 80°C. 500 mg potassium persulfate was added and stirred until the precipitation of the polymer occurs. The precipitated polymer was filtered, washed with water, soxhlet extracted with methanol and was dried in the oven. 5, 10, 15, and 20 mole percent crosslinked polyacrylamide were synthesized using the same procedure.

Conversion of 2mol% HDODA-Crosslinked Polyacrylamides to poly[N-(2-aminoethyl) Acrylamide]

To 10 g of crosslinked polyacrylamide, ethylenediamine (100 mL) was added with stirring and the mixture was heated at 90°C. for 20 hours. The polymer was formed when the reaction mixture was poured into 500 mL of water containing crushed ice. The filtered polymer was made free of unreacted ethylenediamine by washing it with 0.1 M NaCl solution which was indicated by the absence of blue colour formation with ninhydrin reagent. The polymer was then washed with water and methanol and dried. A deep blue color of the polymer when heated with an alcoholic ninhydrin solution, indicated the presence of free amino groups.

100 mL 0.2N HCl was added to 5 g of the aminated polymer and mechanically shaken for 10 hours. The polymer was filtered, washed with water to make it free of acid and methanol, and dried under vacuum.

Conversion of 2mol% HDODA-Crosslinked poly[N-(2-aminoethyl) Acrylamide]

to Polyacrylamides-Supported Chromate Polymers¹⁵

To convert the protonated amino polyacrylamide polymer to polyacrylamides-supported chromate, 5 g of the polymer was suspended in 10 ml of water. 5 g CrO₃ dissolved in water was added, and the mixture was shaken for 10 hours. To completely remove excess CrO₃ the polymer was thoroughly washed with water till free of chromate ions. The polymer was then washed with methanol and acetone and dried in vacuum.

100 mg of chromate functionalised polymer was suspended overnight in 10 ml of 2N NaOH with occasional shaking. The suspension was treated with 5 mL of 10% KI solution and 3 ml conc. HNO₃. Diluted to 50 mL and titrated against standard sodium thiosulfate using starch as the indicator. Chromate functionality of the polymer was calculated from the data obtained.

Oxidation Reactions using Crosslinked Polyacrylamide Supported Chromate: General Procedure

5-fold excess of the water-moistened reagent was added to 100 mg of the substrate, benzoin dissolved in 20 mL of THF, CHCl₃ or cyclohexane, refluxed for the indicated time (Table.1). TLC technique was adopted to monitor the progress of the reaction and after the completion of the reaction, the polymer was filtered and washed with solvent. The solvent was evaporated to get the product.

Investigation of the Correlation between Degree of Crosslinking and Extent of Oxidation

HDODA crosslinked PAs with different mole percent (2, 5, 10, 15, and 20) crosslinks were prepared and functionalized with CrO₃. Benzoin to benzyl oxidation was taken as the model reaction to study the effect of cross-linking on the degree of oxidation. The general steps are as follows:

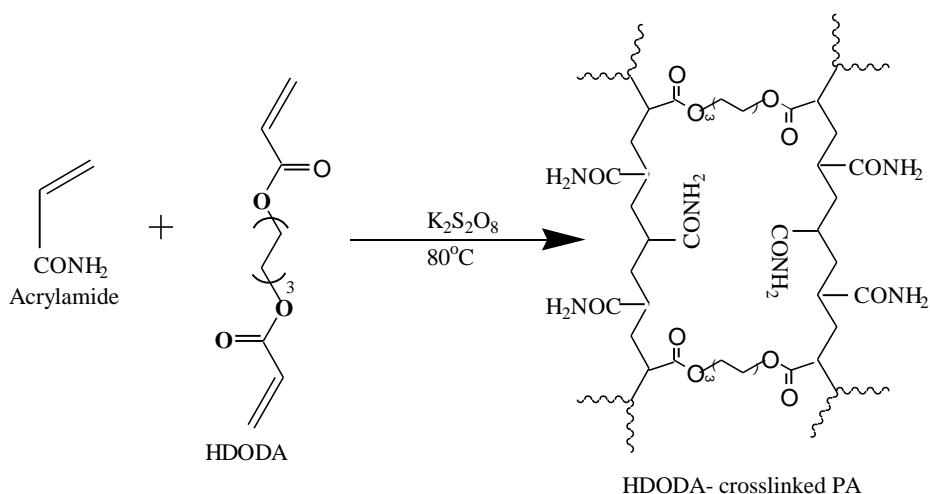
5-fold excess of the water-moistened reagent was added to 100mg of the substrate, benzoin dissolved in 20 mL of THF or cyclohexane (10 mL) and refluxed. 0.1 ml reaction mixture was pipetted out at specific time intervals using a micropipette and made up to 5 ml using the appropriate solvent. The concentration of benzyl was measured with a UV spectrophotometer at 387 nm. The experiment was repeated using different cross-linked polymers.

The Recycling and Reuse of Spent Reagents

For the purpose of eliminating residual organic substrate or products from polymers used in various oxidation reactions, chloroform was used to wash them thoroughly. After being washed, the polymer was treated with HCl (2N) and NaOH (2N), washed with distilled water (2 x 100 mL), and then with acetone. After treating the PA supported chromates with CrO_3 in water at room temperature, the polymer was regenerated. After filtration and washing with water, the filtrate became colorless.

3. RESULTS AND DISCUSSIONS

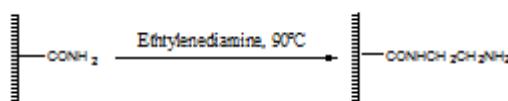
The chromate-supported polyacrylamides of different crosslink densities were synthesized in order to determine the correlation between the structure and reactivity. Free radical solution polymerisation using benzoyl peroxide as the radical initiator was adapted to prepare HDODA-crosslinked polyacrylamides.



Scheme 1. Preparation of HDODA-crosslinked polyacrylamide¹⁶

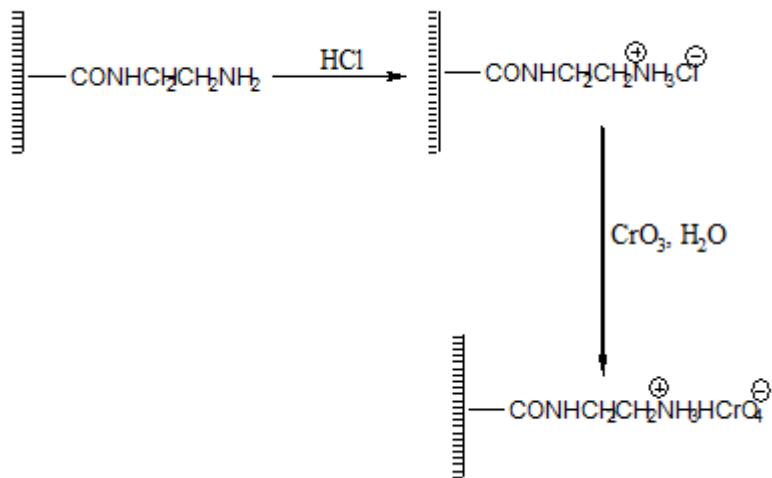
Ethanol was used as the solvent for the monomer mixture and the initiator and the mixture was heated to 80°C. Polymer precipitation was carried out by stirring the mixture, followed by filtering, washing with water, soxhlet extraction with methanol and drying at 50°C.

Transamidation of HDODA-crosslinked polyacrylamides using excess ethylenediamine¹⁷ was carried out at 90°C for 15h (Scheme.2)



Scheme.2. Preparation of Aminofunctionalised PA

Chromates supported polyacrylamides were prepared from amino-functionalized polyacrylamides. Amino-functionalized polyacrylamide was treated with HCl to convert it to the corresponding hydrochloride, swollen in water and treated with an aqueous CrO_3 solution. The reaction mixture was shaken at 0° C. for 2 hours and at room temperature for 4 hours (Scheme. 3). The polymer was washed with water until it was free of CrO_3 , rinsed with methanol, and then rinsed with acetone and dried under vacuum to yield a dark brown polymer.


Scheme.3. Preparation of PA-supported Chromate Reagent

At lower and high crosslink densities (2% & 20%), there is difficulty in accessing the active catalytic site due to high/low swelling. In 20% polymer, the relative stiffness of the polymer matrix increases due to high degree of cross-linking. 20% cross-linked polymer showed minimal reactivity as a result of the inaccessibility of the functional groups near the cross-linking site.

Cross-linked polyacrylamide and its chromate complex were characterized by analytical tools such as FT-IR, ^{13}C CP-MAS NMR and scanning electron microscopy. The FT-IR spectra of cross-linked polyacrylamide showed characteristic absorption at 3500 (NH amide), 1660 (C = O amide), and 1445 cm^{-1} (CN_{str.} Amide). HDODA cross-linked polyacrylamides show the absorbance at 1740 and 1100 cm^{-1} indicating the presence of cross-linking agent esters and ethylene oxide bonds.

The chromate-supported polyacrylamide showed absorption by chromate groups at 943, 885, 860, and 765 cm^{-1} in the FT-IR spectra. The intensity of N-H expansion and contraction vibration has been significantly reduced were found at 179.7 (amide carbon), 41.01 and 26.26 ppm (-CH and - CH_2 of acrylamide) correspond to the carbon peaks for cross-linked polyacrylamide. In the spectrum of chromate supported polyacrylamide, these peaks are downfield and appear at 178.34 and 40.09 ppm.

SEM was used to investigate the morphological changes in cross-linked polyacrylamide and to correlate them with molecular structure, reactivity, and physical attributes.

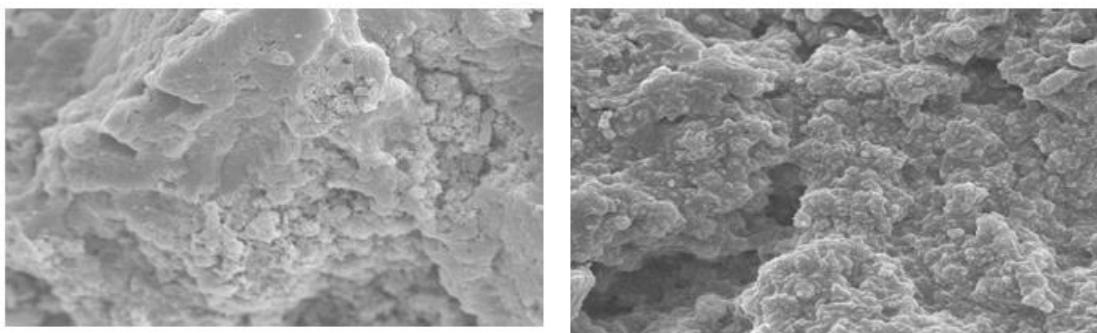


Figure 1: SEM of 10% HDODA Crosslinked PA and PA-Chromate.

The surface of the HDODA crosslinked polymer looks irregular and very porous. Effective swelling and solvation are facilitated by free and proper flow of solvent through a large number of pores on the surface of the polymers as indicated by SEM. A chromic acid base is incorporated during functionalization that results in a rough surface and a reduced porosity.

Oxidation behaviour study of Crosslinked PA-supported Chromates using Primary and Secondary Alcohols

Oxidation of primary and secondary was carried out using 2-20mol% HDODA-crosslinked polyacrylamide supported chromates to study and compare their oxidation behavior. The polyacrylamide supported chromates were moistened with water to enhance the rate of the reaction and Tetrahydrofuran was used as the solvent. Polyacrylamide-supported reagent containing 10 mol% HDODA crosslinked showed maximum oxidation efficiency towards secondary and primary alcohols. The reactivity increased up to 10% and then gradually decreased as the degree of cross-linking further increased.

Table 1: Oxidations using 10% HDODA Crosslinked PA-Chromates

Sl. No	Substrate	Product	HDODA	
			Time	Yield
1	Benzyl alcohol	Benzaldehyde	37	90
2	4- hydroxyl benzyl alcohol	4- hydroxyl benzaldehyde	42	88
3	4-nitro benzyl alcohol	4-nitro benzaldehyde	41	89
4	Cyclohexanol	Cyclohexanone	38	88
5	p- hydroquinone	1,4-Benzoquinone	38	86

Correlation between Degree of Crosslinking and of Crosslinked PA-Supported Chromate Reactivity

Polyacrylamide crosslinked with 10% HDODA demonstrated a greater solvent intake capability among the five different crosslinked chromate supported polymers.

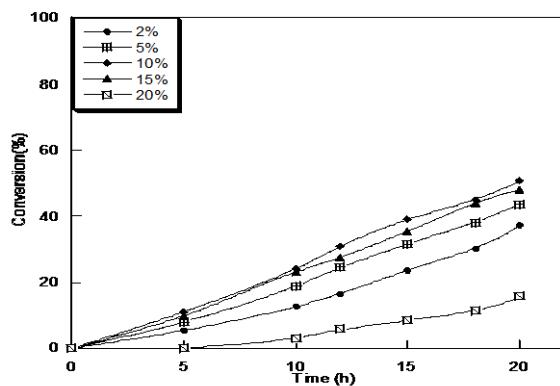


Figure 2: Reactivity of Crosslinked PA-Supported Chromate- Effect of Crosslinking.

10% HDODA crosslinked polyacrylamide supported chromates exhibits maximum efficiency and on increasing the degree of crosslinking, reactivity decreases progressively. Several researchers have studied the relationship between the type and degree of cross-linking of polyacrylamide supported reagents and observed their non-linear relation in reactivity.¹⁸

CONCLUSIONS

A set of HDODA crosslinked polyacrylamides of varying crosslink density was prepared and they were converted to polymeric chromate derivatives. In order to correlate the structural parameters with reactivity, oxidation of five different compounds were carried out and their chemistry was investigated. 10% HDODA-crosslinked polyacrylamide-supported chromates system exhibited maximum efficiency. Low molecular weight reagents diffuse into the polymer matrix at a slower rate, resulting in an increase in the reactivity of up to 10%. Crosslinking agents can be selected properly and crosslink density can be adjusted to tailor a polymeric reagent and create a specific microenvironment necessary to induce specificity and selectivity at the reaction site.

REFERENCES

1. Prabhakaran, P.V.; Venkatachalam, S.; Ninan, K.N. *Eur. Polym. J.* **1999**, 35, 1743.
2. Sreekumar, K.; Pillai, V.N.R. *Polymer* **1987**, 28, 1599.
3. George, B.K.; Pillai, V.N.R. *Polymer* **1989**, 30, 178.
4. Haridasan, V.K.; Ajayaghosh, A.; Pillai, V. N.R. *J. Org. Chem.* **1987**, 52, 2662.
5. Frechet, J.M.J.; Haque, K.E. *Macromolecules* **1975**, 8, 130.
6. S. Sumi Mitra, K. Sreekumar, *Designed Monomers and Polymers*, 1999 2:2, 153-163
7. Renil, M; Nagaraj, R; Pillai, V.N.R.; *Tetrahedron*, **1994**, 50, 6681.
8. Mathew, B.; Pillai, V. N. R. *Polymer* **1993**, 34, 2650.
9. George, B.; Mathew, B.; Pillai, V. N. R. *J. Appl. Polym. Sci.* **1999**, 74, 3432.
10. Gigimol, M. G.; Jose, J.; Mathew, B. *J. Macromol. Sci: Pure Appl. Chem.* **2006**, 43, 689.

11. George, B. K.; Pillai, V. N. R. *J. Polym. S: Part A: Polym Chem.* **1990**, 28, 2585.f
12. Jose, L.; Pillai, V. N. R. *J. Appl. Polym. Sci.* **1996**, 60, 1855.
13. Caulfield, M. J.; Qaio, G. G.; Solomon, D. H. *Chem. Rev.* **2002**, 102, 3067.
14. Thomas, S. *Int. j. innov. res. adv. Stud.* **2016**, 3, 8,100-105.
15. Thomas, S. *Int. j. innov. res. Technol.* **2016**, 5,7, 13587-96
16. Suma Bino Thomas, *Ph.D Thesis, Mahatma Gandhi University, Kerala, India, 2009*
17. Inman, J. K.; Dentzis, H. M. *Biochemistry* **1969**, 8, 4074.
18. Devaky, K. S. *Ph.D Thesis, University of Calicut, Kerala, India, 1989*.
19. Bedjargi, Pruthvi Raj C., and RS Kulkarni. "SDS-Page Analysis and Electron Microscopy of Corpuscles of Stannius Secretion in the Freshwater Fish, *Notopterus Notopterus*." *International Journal of General Medicine and Pharmacy (IJGMP)* 3 (2014): 1-6.
20. Aggarwal, Anupriya, and Praveen Kanth. "DNA encryption." *International Journal of Computer Science and Engineering (IJCSE)* 3.3 (2014): 51-66.
21. Sankaran, Saravanan, et al. "Isolation and optimization of constitutively synthesized invertase, from *Saccharomyces cerevisiae* mutant type strain." *Int J Appl Nat Sci* (2017).
22. Capek, Ignác. "Gold Nanoparticles in Cancer Cell Lines." *International Journal of General Medicine and Pharmacy (IJGMP)* Special Edition: 1-14.
